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Degradation of organophosphorus pesticide induced by oxygen plasma: Effects of operating parameters and reaction mechanisms

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ABSTRACT

The degradation effectiveness and degradation mechanism of representative organophosphorus (OP) pesticide during oxygen plasma treatment have been studied. The identification and quantitative determination of OP pesticide, the degradation mechanisms for OP pesticide destruction, its destruction intermediates, and by-products were performed using gas chromatography/mass spectrometry (GC/MS). Plausible mechanisms of the degradation are discussed. Experimental results indicate that oxygen plasma treatment has noticeable effects on OP pesticide with satisfactory degradation efficiency, which mainly depends on related operating parameters including plasma treatment time, discharge power, distance from the center of the induction coil, and concentrations of OP pesticide. It was found that OP pesticide was degraded into less-toxic compounds, and free radical reaction and addition reaction were to be the dominated the degradation mechanisms for OP pesticides treated by oxygen plasma. Therefore, our results suggest that oxygen plasma is suitable for degradation of OP pesticide.

1. Introduction

Organophosphorus (OP) pesticides have been widely used as an alternative to organochlorine compounds for the control of insecticide in a wide range of fruit, vegetables, and grain all over the world. The consequences of OP pesticides use on natural ecosystems were one of the first important issues in the field of environmental chemistry. Due to their extensive use and moderate persistence, OP pesticide residues could be found on commodities at the time of sale and natural waters (Bai et al., 2006; Ambrus, 2009; Hernandez-Borges et al., 2009). The impact of OP pesticide molecules on the environment result from several factors: the toxicity, the bioaccumulative and long-term effects, and the transport between different compartments (Lotti, 2002; Costa, 2006; Gupta et al., 2007; Lu et al., 2008; Palma et al., 2009). Moreover, it has recently been determined that by-products of transformation in the environment can play a significant role in defining the impact of pesticides on both human health and the natural ecosystems (Goncalves et al., 2006; Mitsou et al., 2006). In many cases, the combined effects of multisite use of several pesticides in mixtures may lead to augmentation of toxicities mentioned above, i.e. synergistic effects (Dekundy et al., 2007). In order to avoid potential human exposure to OP pesticide residues via food and drinking water, the effective techniques to remove and degrade pesticide residues for health purposes is badly needed. Some conventional methods have been used for the degradation of OP pesticide residues such as photolysis, hydrolysis, ozonation, ultrasonic irradiation, and ionizing radiation (Schramm and Hua, 2001; Evgenidou et al., 2006; Basfar et al., 2007; Le Person et al., 2007; Oancea and Oncescu, 2008; Ormad et al., 2008). However, the removal efficiency of these techniques is somewhat limited and undesired toxic compounds are sometimes formed as well. Therefore, developing an alternative approach to overcome the above mentioned problems turns to be a necessity.

Non-thermal plasma (NTP), such as dielectric barrier discharge (DBD), corona discharge, and glow discharge, is a highly potential alternative for degradation of OP molecules in some literature (Chen Clothiaux et al., 1984; Guo et al., 2007; Kim et al., 2007; Cho et al., 2008; Chen et al., 2009). However, there is little information available in literature about degradation of OP pesticides treated by non-thermal plasma, and the degradation mechanisms have not been fully understood. The main characteristic of NTP is its high energy electron temperatures (10^4–10^5 K), i.e. the average electron energy is in the range of 0–10 eV, whereas the bulk gas temperature remains as low as room temperature (Suhr and Pfreundschuh, 1988). All organic molecules having similar ionization and dissociation energies (3–6 eV), can easily be destroyed by NTP, in which high energy primary electrons collide with the molecules of the feed gas to form secondary electrons and highly reactive species by the mechanisms of ionization, excitation and dissociation (Suhr, 1983; Patiño et al., 1995). When OP pesticide

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molecules are exposed to the plasma under selective experimental conditions, high energy electrons generated from plasma can provide sufficient energy to dissociate the molecules of the feed gas or OP pesticide, and then produce free radicals including radicals (e.g. ·O, ·OH) and excited species initiated the chemical reactions, which are normally not possible to occur at low temperatures. Accordingly, the chemical bonds of OP pesticide can be effectively broken and various desired conversion of OP pesticides are performed to liberate unharmful or less hazardous compounds. In addition, UV and irradiate light derived from NTP can also boost the degradation efficiency of OP pesticides. As a result, physical conditions and chemical reactive species in NTP are regarded as a comprehensive process for rapid and efficient degradation of OP pesticide. This implies relatively lower energy consumption used for operating the reaction system without causing secondary pollution compared to the conventional degradation processes.

As one of the largest agricultural countries, China is a major user of OP pesticides in the world. Even though the use of OP pesticides has been restricted drastically by the officially rigorous regulations, over 10,000 tons of Dichlorvos (DDV) (*O*-2,2-dichlorovinyl-*O*,*O*-dimethylphosphate, $C_4H_7Cl_2O_4P$, $M = 220.99\ g\ mol^{-1}$ – CAS Registry No. 62-73-7) is still applied annually in China. Besides the above-mentioned toxicities, it has been reported that human exposure to DDV leads to the disorder of glucose metabolism and causes hyperglycemia as well (Romero-Navarro et al., 2006). Furthermore, DDV has been classified by the United States Environmental Protection Agency (US EPA, 1988) as a toxic chemical in the Toxics Release Inventory (TRI). For this reason, DDV was selected as a representative target OP pesticide in this study.

The objective of this research were to apply the approach based on the determining and assessing the degradation effectiveness and using the obtained data for discussion of possible mechanism of the degradation of DDV during oxygen plasma treatment. The effects of operation parameters including plasma treatment time, discharge power, distance from the center of the induction coil, and concentrations of DDV were investigated using GC. To elucidate the major plasma degradation reactions as well as the degradation mechanisms for DDV destruction, its destruction intermediates and by-products were performed using GC/MS. To the best of our knowledge, this is the first time to study oxygen plasma degradation of DDV and reveal the chemical reaction and plasma degradation mechanisms. Therefore, this research will enrich the potential application of NTP to remove toxic organic materials from environment based on its significant advantages such as its independence of chemicals, high efficiency and low cost for the degradation of OP pesticide.

2. Experimental

2.1. Reagents and materials

DDV standard (99.0–99.5% purity) was provided by the Institute of Environmental Protection and Monitoring, the Ministry of Agriculture, of China. The stock solutions of DDV were prepared in acetone at concentration of $100\ \mu g\ mL^{-1}$. The solutions, stored without exposure to light in the refrigerator at 4 °C, were utilized within 12 h after they were made to ensure that no degradation occurred prior to oxygen plasma treatment. All organic solvents were purchased from Xi'an Chemical Co. and re-distilled before using.

2.2. Apparatus

Fig. 1 shows the schematic diagram of the plasma treatment system employed in this work. This system consists of four parts: gas inlet, reaction chamber, vacuum pump, and power supply (SY-500 W 13.56 MHz) and matching network (SP-II matcher) which are made by the Science Academy of China. The reaction chamber is a cylindrical Pyrex glass tube (1000 mm in length and 45 mm at diameter), where inductance-coupling discharge is applied. The Pyrex glass tube has a copper coil for the energy input of radio frequency (RF) power (13.56 MHz frequency), which is adjusted by a power controller.

2.3. Plasmas degradation reaction testing procedure

In the first test series, $100\ \mu g\ mL^{-1}$ standard solution of DDV was spin-coated onto glass slides (20 mm × 20 mm) with two different levels of 20 and 100 μL, respectively, (i.e. corresponding to the initial deposited dose of DDV at low concentration and high concentration). The samples were positioned onto a glass plate (100 mm × 35 mm) at the constant distance of 0, 20, 40, 60, and 80 cm from the center of the induction coil in the Pyrex glass tube of the reactor and they were exposed to the oxygen plasma. First, the reactor is evacuated to approximately 10 Pa, and then oxygen gas was injected into the Pyrex glass tube at difference flow rate. The working pressure of 50 Pa in the plasma reactor is adjusted through mass flow controllers. The oxygen plasma was operated at discharge power levels of 30, 60, 90 and 120 W for given time

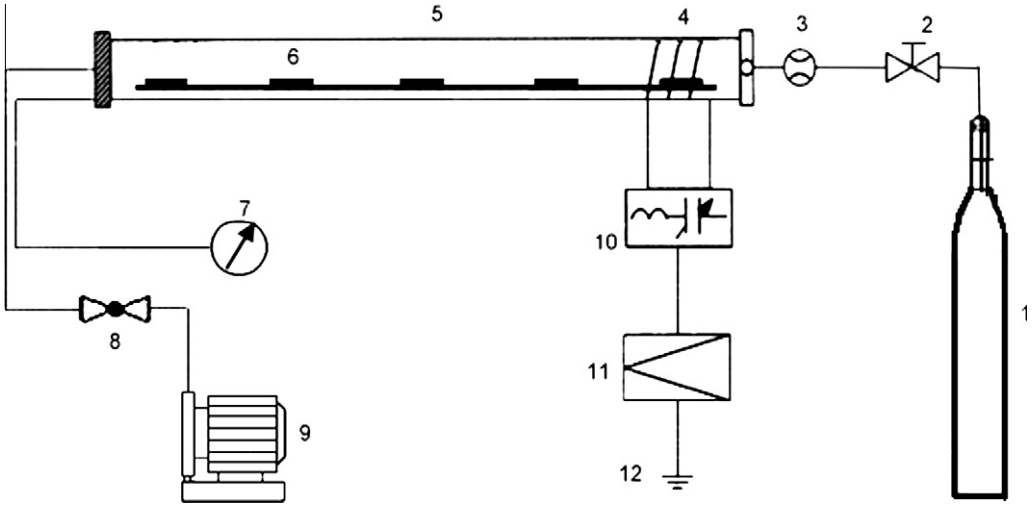

Fig. 1. Schematic representation of the experimental apparatus employed in the plasma degradation of the DDV (1) gas bottle; (2) valve; (3) mass flow meter; (4) inductance coil; (5) reaction chamber; (6) sample; (7) vacuum gauge; (8) electromagnetic valve; (9) vacuum pump; (10) matching system; (11) rf generator; (12) grounding protection.

of 30, 60, 90 and 120 s with different oxygen flow rate. After plasma treatment, each sample was withdrawn from the plasma reactor immediately and dissolved in an ultrasonic bath of acetone for 5 min, with a metered volume at 2.0 mL for GC analyses. Meanwhile, the studied variables including discharge power, plasma treatment time, oxygen flow rate, distance from induction coil, and concentrations of pesticide on the degradation of DDV were determined. Every other sample was manipulated three times to ensure the reproducibility. The degradation efficiency of DDV was described with the degradation fraction η, which was calculated from the following equation: $\eta = [(C_0 - C_t)/C_0] \times 100\%$, where η is the degradation fraction; C_0, the initial concentration of DDV prior to plasma treatment; and $C_0 - C_t$ is the removal concentration of DDV at a give plasma treatment time. The influence on DDV degradation efficiency under different plasma treatment parameters were assessed for comparison.

In the second test series, in order to investigate the plasma degradation mechanisms for pesticides, the initial high concentration of DDV was selected to provide favorable conditions and facilitate the identification of intermediates and by-products. The other optimum plasma degradation parameters based on the first test series were selected as the treatment conditions in this series. Identification of intermediates or products was performed by GC/MS.

GC conditions: a shimadzu-2010 gas chromatograph (GC) equipped with a flame photometric detector (FPD) and RTX-225 high performance capillary columns 30 m × 0.32 mm × 0.25 μm; injector temperature and detector temperature were 250 °C and 280 °C, respectively; the rate of the temperature rise is 70 °C (1 min)→30 °C min^{-1} → 170 °C (3 min) → 4 °C min^{-1} → 225 °C → 25 °C min^{-1} → 250 °C (1 min); GC/MS conditions: an Agilent Technologies 6890 gas chromatograph, equipped with an HP-5MS column (30 m × 0.25 mm i.d. × 0.25 μm) coated with 5% phenyl 95% methylpoly-siloxane, coupled to an MSD 5973 selective mass detector (Agilent Technologies). MS conditions: electron energy 70 eV, collect current 300 μA, source temperature 150 °C. Identification and confirmation of the pesticides were based on their retention times and the comparison of their sample mass spectrum with the characteristic ions in the standard mass spectra.

As one of the major final products of DDV, the formation rate of phosphate can also be used to assess the degradation level of DDV during oxygen plasma process. Therefore, we examined the recovery of phosphate with the ammonium molybdate spectrophotometric method (Chinese National standard method/GB 11893-1989) in this study. At this point, the plasma degradation efficiency of DDV is expressed by phosphate recovery percent as the following expression: $\eta = (P_t/P_0) \times 100\%$, where η is phosphate recovery percent; P_t, the formed concentration of phosphate after plasma treatment time t; and P_0 is the total concentration of organophosphate. In this experiment, the samples with high concentration of DDV were positioned in the discharge zone (0–20 cm), afterglow zone (20–60 cm) and remote zone (60–80 cm) during plasma treatment.

2.4. Statistical analysis

Quality control and quality assurance measures were incorporated in the analytical scheme. The study on effects of variables plasma treatment conditions including discharge power, plasma treatment time, oxygen flow rate, distance from induction coil, and concentration of pesticide on the degradation of DDV were designed based on preliminary orthogonal experiment. Every sample was manipulated three times to ensure the reproducibility and the results were statistically analyzed. Data were statistically evaluated by one-way analysis of variance (ANOVA) with SPSS 13.0 software. When significant differences were found at a 95% confidence level ($p < 0.05$), the least significant difference (LSD) test was performed among means.

3. Results and discussion

The degradation efficiency of DDV during oxygen plasma treatment as a function of plasma treatment time, plasma discharge power, oxygen flow rate, and distance from induction coil were investigated with the degradation fraction. DDV residues were determined using GC with retention time at the mentioned GC conditions. Different initial DDV concentrations were also employed to examine how the initial DDV concentrations affect the degradation efficiency.

3.1. Effect of plasma treatment time

The degradation fraction of DDV as a function of plasma treatment time at the distance mentioned previously was shown in Fig. 2. In this case, applied discharge power was 120 W and oxygen flow rate was 40 cm^3 min^{-1}. It is clearly shown that the degradation fraction increases with the increase of plasma treatment time regardless of the sample position both at low and high concentration of DDV. Almost 100% conversion of DDV at low concentration

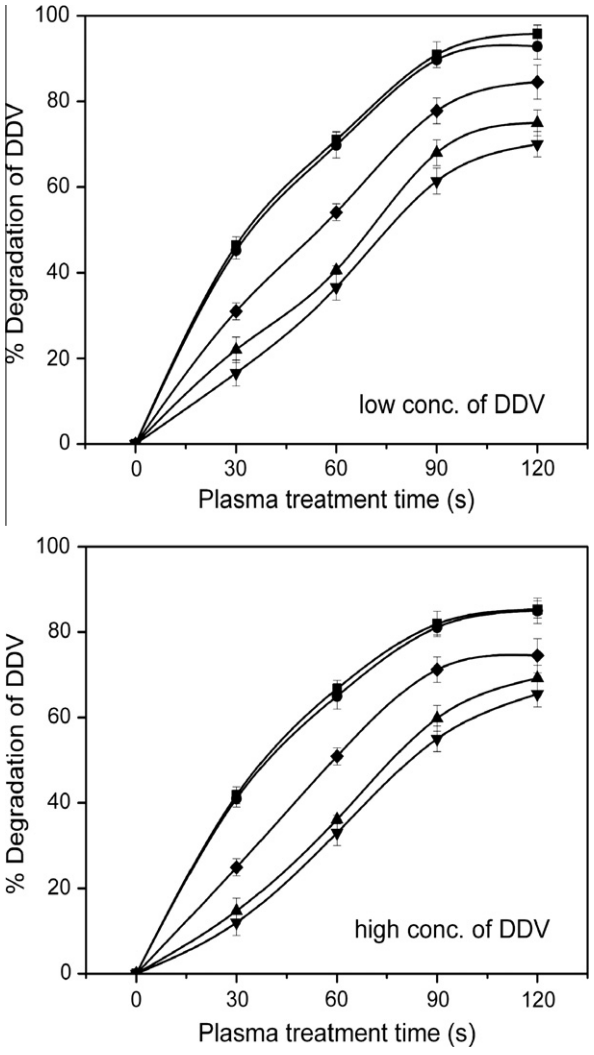

Fig. 2. Effect of plasma treatment time on degradation of DDV at distance of (●) 0 cm; (■) 20 cm; (□) 40 cm; (▲) 60 cm; (▼) 80 cm. Applied discharge power: 120 W; O_2 flow rate = 40 cm^3 min^{-1}.

is achieved in discharge zone (0–20 cm) when treatment time exceeds 120 s, whereas the lower destruction efficiency at high concentration was observed in the remote zone (60–80 cm). The results indicate that plasma treatment time is an important parameter that can influence the degradation efficiency of DDV. The interaction involving pesticide molecules and reactive species has almost completed within 120 s, and longer plasma treatment time could speed the degradation of DDV. Furthermore, one remarkable influence is concentration of DDV, i.e. the plasma degradation fraction of DDV is more noticeably high at low concentration than that at high concentration with statistical significance ($p < 0.05$) at all exposure time (Fig. 2). This has important implications in practical situations because the control time required to lower the concentration of any pesticide will affect cost. Thus, plasma treatment time and concentration of pesticides were the important factors for degradation of DDV.

3.2. Effect of discharge power

The degradation fraction of DDV versus discharge power is plotted at the above mentioned distances for plasma treatment time 120 s and oxygen flow rate 40 cm^3 min^{-1} (Fig. 3). It is interesting to mention the diminution of its degradation as discharge power varied from 30 to 60 W. Further increasing discharge power enhances the degradation of DDV, and then it tends to remain stable beyond 90 W. Therefore, the degradation efficiency undulates with the increase of the discharge power. The different effects can be related to the average energy of reactive species which are increasing with the enhancement of the discharge power in the range for 0–30 W, and subsequently, a different fall trend appears (30–60 W). Over 90 W, the probability of each reaction species colliding with pesticide enhances; so, degradation increases. In addition, the degradation efficiency of low concentration of DDV at 120 W was greatest in the discharge zone (0–20 cm), but it was the least effective at 60 W in the remote zone (60–80 cm) for high concentration of DDV. ANOVA analysis also indicates that the degradation fraction of DDV was significantly higher in discharge power treatments conducted at 30, 90 and 120 W than 60 W with statistical significance ($p < 0.05$), but not in the case of 30 and 90 W, of 30 and 120 W, and of 90 and 120 W ($p > 0.05$). At this point, the results agree well with the findings in our prior study (Li, 2006). In our previous investigation, we observed a similar trend for the overall power levels which depend on the density and amount of all created reactive species in plasma inner electronic field; i.e. when the discharge power range from 0 to 30 W, the electron energy is increased to remain the peak values of 11.0 eV as the distance increased to 20 cm. As a result, the possibility for DDV molecule to experience the dissociation by collision with electrons is enhanced and their interaction is promoted as well. When the discharge power varied from 30 to 60 W, the relative high recombination rate of electrons leads to the plasma inner electronic field becoming weak, consequently the remained electrons are not able to carry the necessary energy to perform a dissociation collision and the average energy of mass of reactive species (secondary electrons and radicals) reduces along with the probability of degradation reactions. However, it can balance out the recombination rate of electrons with the further increases of the discharge power. Therefore, the average energy of electrons can extend the action sphere within the plasma inner electronic field.

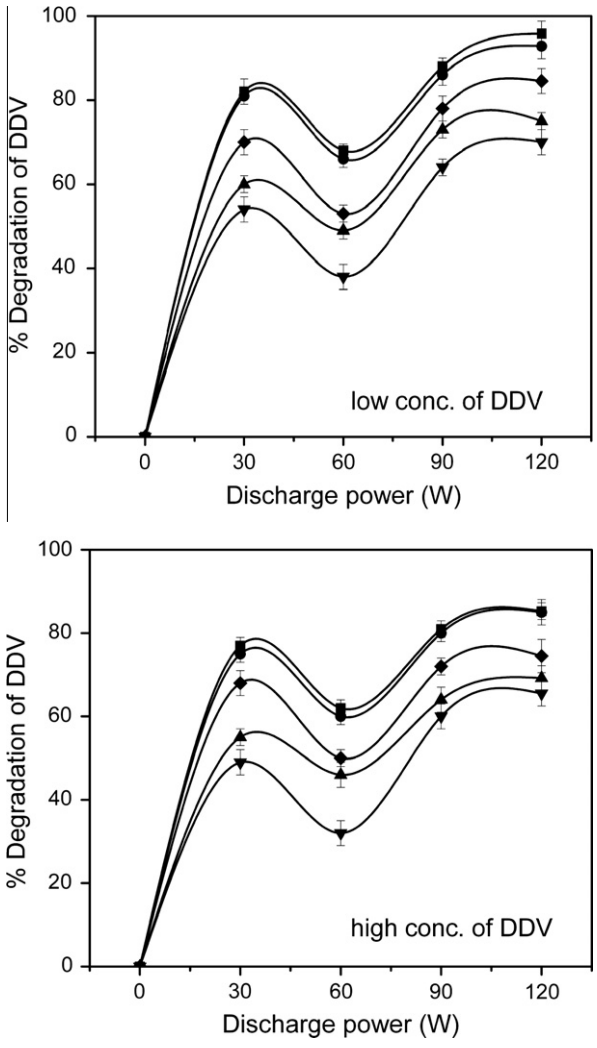

Fig. 3. Effect of discharge power on the degradation of DDV at distance of (●) 0 cm; (■) 20 cm; (□) 40 cm; (▲) 60 cm; (▼) 80 cm. Applied plasma treatment time: 120 s; O_2 flow rate = 40 cm^3 min^{-1}.

According to the above results, it can be concluded that electrons are the main source of dissociation in a plasma process and the average power of the electrons greatly impacts the formation of radicals which give rise to the decomposition of pesticide. A series of less-toxic molecules than the parent pesticide molecules is liberated as a result. In addition, the treatment time and discharge power are equally important for the reduction of DDV. The maximum degradation fraction of DDV is obtained during oxygen plasma treatment for 120 s at 120 W. For the subsequent investigation of the effects of oxygen flow rate on degradation of DDV, we fix these two plasma treatment conditions.

3.3. Effect of oxygen flow rate

Fig. 4 displays the variation in the degradation fraction of DDV over oxygen flow rate at above-mentioned distance for 120 s at 120 W. The degradation increases firstly but decreases later with the increase of oxygen flow rate at all distance. For the same reason, when discharge power and plasma treatment time are fixed, the constant energy is obtained in the reaction system. Thus, the different effects can be related to the average energy of reactive species, which is enlarged with increasing oxygen flow rate from 20 to 40 cm^3 min^{-1}, and subsequently different drawdown appears (40–100 cm^3 min^{-1}). ANOVA analysis also indicates that plasma degradation fraction of DDV is more noticeably high at 40 cm^3 min^{-1} than other oxygen flow rate with statistical significance ($p < 0.05$), but not in the case of 20 and 60, 80 and 100 cm^3 min^{-1} ($p > 0.05$). Therefore, oxygen content also affects the degradation efficiency of DDV. Similarly, as the oxygen flow rate increased from 20 to 40 cm^3 min^{-1}, the number of reactive

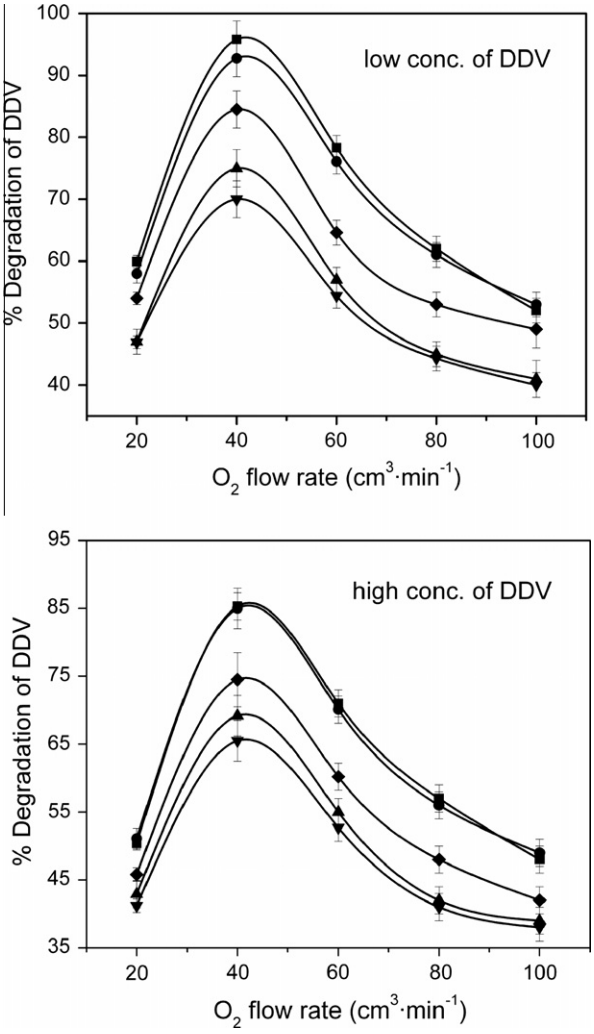

Fig. 4. Effect of oxygen flow rate on the degradation of DDV at distance of (●) 0 cm; (■) 20 cm; (□) 40 cm; (▲) 60 cm; (▼) 80 cm. Applied discharge power: 120 W; plasma treatment time: 120 s.

species also increases. As a result, the probability of reactive species collision with pesticide is enhanced and degradation boosts as well. At high oxygen flow rate exceeds 40 cm^3 min^{-1}, the density of reactive species is large but the average energy and residence time is relatively low, so the probability of reactive species collision with pesticide molecules is comparatively small, consequently the degradation reaction declines. It is concluded that the degradation efficiency of pesticide molecule exposure to plasma is the combining effects relying on the average energies and the amount of reactive species, and their residence time.

All these values in Figs. 2–4 indicate that the optimum oxygen plasma degradation conditions for DDV are discharge power of 120 W, plasma treatment time of 120 s and oxygen flow rate of 40 cm^3 min^{-1}. The subsequent investigation should be taken under these optimum plasma treatment conditions.

3.4. Effect of distance from the induction coil

Fig. 5 displays the degradation fraction of DDV both at low and high concentrations under the optimum degradation conditions against the distance from induction coil. In general, a decline in the plasma degradation of DDV is observed as the distance increase both at low and high concentrations. When other conditions are maintained constant, the degradation fraction of DDV at low and

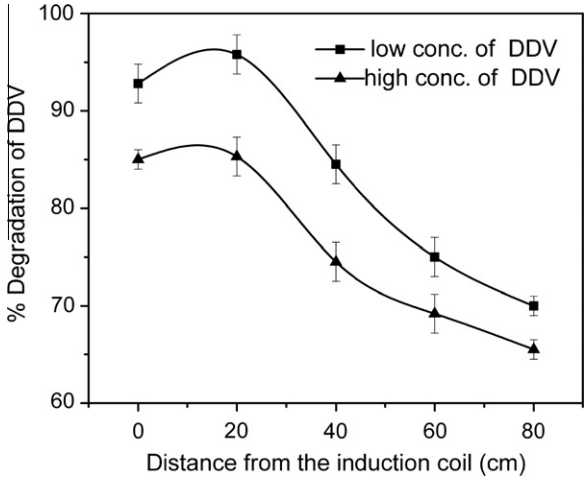

Fig. 5. The effect of the distance from the induction coil on DDV degradation of different concentration. Applied discharge power: 120 W; plasma treatment time: 120 s; O_2 flow rate = 40 cm^3 min^{-1}.

high concentrations ranges from 70% to 96% and from 65% to 85% respectively. Therefore, the treatment was less effective at high concentration than that at low concentration with statistical significance ($p < 0.05$). It was also found that degradation of DDV by oxygen plasma is much higher in the discharge zone (0–20 cm) than that in the remote zone (60–80 cm) with statistical significance ($p < 0.05$), but there is no difference within discharge zone (0–20 cm), afterglow zone (20–60), and remote zone (60–80 cm) ($p > 0.05$). In our prior research (Bai, 2009) it was verified that the intensities of various species including electrons, ions, and free radicals were decreased with increasing distance from the discharge zone to the remote zone; i.e. a mass of various reactive species (electrons, ions, free radicals, etc.) exist in the discharge zone, while there are only free radicals in the remote zone. This happens because the different life-spans of various reactive species due to the different rate constants of recombination and dissociation reactions between electrons and ions of 10^{-7} cm^3 s^{-1}, free radicals and free radicals of 10^{-33} cm^3 s^{-1} respectively (Goldman and Amouroux, 1983). Therefore, it could be explained that the intensity of reactive species (electrons, ions, radicals, etc.) in the discharge zone is higher than that in the afterglow zone and the remote zone, subsequently facilitating the degradation of pesticides in the discharge zone. We can see that among the whole plasma degradation treatment, electrons and radical affect the degradation of pesticide together. In addition, it can not be ignored the fact that a certain amount of DDV may be reduced through evaporation besides degradation in this oxygen plasma process.

3.5. Identification of by-products and possible degradation mechanisms

In order to explore the possible degradation mechanisms of DDV, it is very important to identify the intermediates and by-products during plasma treatment. The optimum plasma degradation conditions (discharge power of 120 W, plasma treatment time of 120 s and oxygen flow rate of 40 cm^3 min^{-1}) at high concentration of DDV were achieved to evaluate the effect of operating parameters on the products distribution and degradation pathways in this investigation. GC/MS analyses indicate that the plasma degradation of DDV yield three organic intermediates. Compound (1) was identified as *O*,*O*-dimethyl phosphonic ester (more than 90% matching) with the retention time of 3.82 min and the ions at *m*/*z* 109, 79, 80, and 79. The ions at *m*/*z* 109 and 79 are charac-

teristic of the phosphate esters and belong to the groups $[(CH_3O)_2P(O)]^+$ and $[CH_3O–P–OH]^+$ respectively. Compound (2) was identified as 2,2-dichlorovinyl *O*-methylphosphate (more than 70% matching) with the retention time of 4.73 min and exhibited the $[M]^+$ ion at *m*/*z* 207 that corresponds to the loss of a methyl group (M−14) from DDV, and the characteristic ions of $[CH_3OP(OH)_2]^+$, $[CH_3OP(O)OH]^+$, $[CH_3O–P–OH]^+$, $[P(OH)_2]^+$ and $[OP–OH]^+$ at *m*/*z* = 96, 95, 79, 65 and 64 respectively. Compound (3) was identified as *O*,*O*,*O*-trimethyl phosphoric ester (more than 70% matching) with the retention time of 5.12 min and exhibited the $[M]^+$ ion at *m*/*z* = 140, 110, 95, 79 that belong to the groups $[(CH_3O)_3P(O)]^+$, $[(CH_3O)_2P(OH)]^+$, $[CH_3OP(O)OH]^+$, and $[CH_3O–P–OH]^+$, respectively. They are also identified as intermediates during decomposition of DDV and other organophosphorous pesticides (Chiron et al., 2000).

Based on the GC/MS diagnosis about distribution of various intermediates and theory of organic chemical reaction mechanisms, a primary reaction mechanism can be proposed for the oxygen plasma degradation of DDV. It was possible that DDV was degraded during oxygen plasma treatment via two pathways. First route is based on free radical reaction initiated by free radical generated in plasma. Another pathway may be suggested by addition reaction in which the electrons provide energy and impact the reaction involved in unsaturated bonds within DDV molecule as show in Fig. 6. Possibly, both stages take place nearly simultaneously. Concretely speaking, if a DDV molecule is exposed to oxygen plasma, hydrogen abstraction from $CH_3O–$ groups is more probable when ·O free radicals attack DDV molecule, followed by the removal of $–CH_2O$. It leads to the formation of compound (2). When electrons provide the C=C or P=O bond with energies to undergo addition reaction which was initiated by O free radicals to form dimethyl phosphate and dichloro-acetaldehyde, further formed by Cl^-, PO_4^{3-}, etc. Moreover, the cleavage of the dichlorovinyl group proceeds more easily than *O*-demethylation. Similarly one can expect products (1) and (3) to be formed by the reactions during plasma of DDV. In this study, some intermediates are coincident with GC/MS diagnostics and plausible destruction mechanisms in advanced oxidation of DDV are also discussed (Chiron et al., 2000; Pehkonen and Zhang, 2002). In addition, we expect the C–H bond, C–O bond and C–C bond to be broken more readily than the P=O bond and P–H bond based on the different bonds dissociation energies (Chang, 2002). Therefore, this mechanism is based on the physical and chemical processes involving electrons and free radicals. DDV are degraded by oxygen plasma treatment along with the proposed pathways described in Fig. 6.

On the other hand, phosphate recovery was another assessment of the plasma degradation effects of DDV. Fig. 7 shows the phosphate recovery of DDV plasma degradation at high concentration as a function of plasma treatment time at 120 W and oxygen flow rate of 40 cm^3 min^{-1}. It is indicated in Fig. 7 that phosphate recovery increases as plasma treatment time increasing to 90 s in discharge zone (0–20 cm), afterglow zone (20–60 cm) and remote zone (60–80 cm). These differences were statistically significant ($p < 0.05$) in the case of discharge zone, afterglow zone, and remote zone, but not in the case of afterglow zone and remote zone ($p > 0.05$). Results also showed that phosphate recovery of the expected amount of 85% was observed after 90 s in discharge zone. On the contrary, the relatively low efficiency was obtained in afterglow zone and remote zone. This can also be explained that electrons and free radicals dominate the degradation reaction in discharge zone, whereas only free radicals mainly influence the degradation efficiency in afterglow zone and remote zone. These results coincide with the previous results in this study. However, there is a certain amount of analytical error (variation) associated with the measurements, which propagates through the calculations. It is likely that analytical error accounts for some of the calculated recoveries greater than 100%. To the best of our knowledge, there has not been any report regarding the DDV oxygen plasma degradation as a starting compound, thus no comparison of observed degradation products with the literature data could be done.

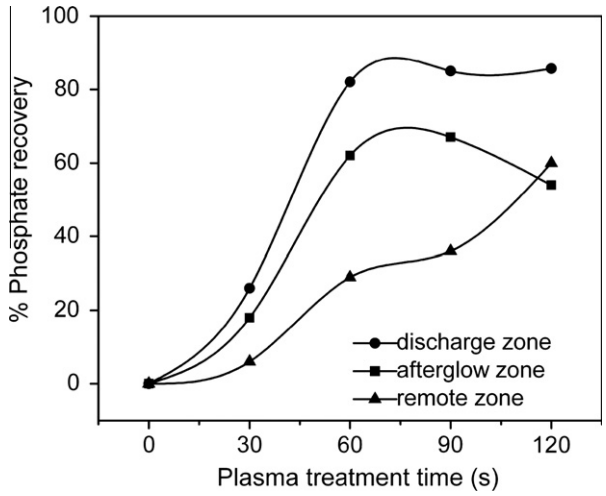

Fig. 7. Phosphate recovery during oxygen plasma degradation of DDV. Applied discharge power: 120 W; O_2 flow rate: 40 cm^3 min^{-1}.

4. Conclusions

The main conclusions can be drawn from the present study:

(1) It was the first time that the determination of degradation efficiency and investigation of the degradation mechanisms of DDV during oxygen plasma treatment were conducted successfully. The reactive species in oxygen plasma are able to degrade DDV completely in a very short exposure time. It

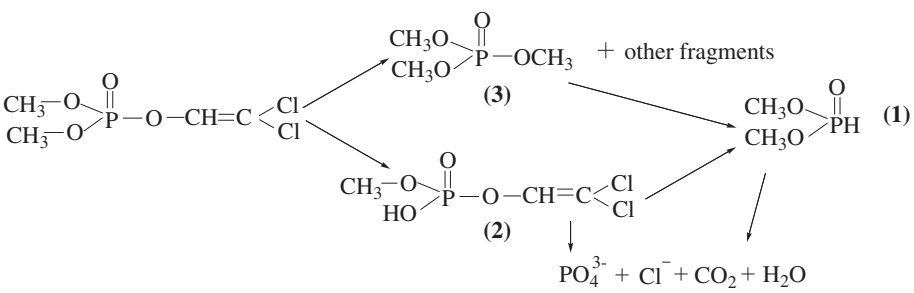

Fig. 6. Degradation of DDV during oxygen plasma treatment. (1) *O*,*O*-dimethyl phosphonic ester; (2) 2,2-dichlorovinyl *O*-methylphosphate; (3) *O*,*O*,*O*-trimethyl phosphoric ester. The "other fragments" were not identified by GC/MS. See text for a discussion.

is clear that the treatment is more effective at relatively lower concentration than at high concentration of DDV. The plasma degradation strongly depends on the related operating parameters and the optimum plasma degradation conditions are plasma treatment time of 120 s, discharge power of 120 W, and O_2 flow rate of 40 cm^3 min^{-1} at the discharge zone.

(2) The oxygen plasma degradation mechanisms of DDV are dominated by high energies electrons and free radicals, which is similar to that of DDV in advanced oxidation. In addition, most of the identified intermediates and by-products are more innocuous than DDV molecule during oxygen plasma treatment.

(3) Even though many questions still remain open, the efficient reduction of DDV by oxygen plasma, demonstrated here, provides an alternative approach to remove of toxic organic materials from environment. Further plasma experiments were dedicated to the elucidation of the chemical kinetics mechanisms and to expand plasma degradation application to a wide range of pesticides.

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